Bioethanol as a possible source of *n*-butanol

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Received: 31 March, 2021 *Accepted: 20 April, 2021*

ABSTRACT

A novel synthesis method was proposed to produce *n*-butanol from bioethanol. The key step is the chemical dehydration of ethanol to ethene. Then ethene is further converted via Wacker synthesis, followed by commercial steps, such as aldol condensation and catalytic hydrogenation to form *n*-butanol. Environmental sustainability assessment of the synthesis method was executed: E-factor was calculated to be 0.8914, atom efficiency to 58.8%. Recently introduced sustainability metric – the Ethanol Equivalent – was used to calculate the carbon-atom and energy requirements of the process. A total 2.66 million tonnes (mt) ethanol would be required to cover the synthesis of 0.67 mt *n*-butanol (used in EU-28 in 2015), which represents about the half of the amount of ethanol produced in the same year. Sustainability value of resource replacement was calculated to be 5.15 (>1), which indicates a sustainable production. Sustainability value of the fate of the waste showed an unsustainable value of 0.49 (<1), due to the relatively low overall yield of the reaction (63%). Sustainability index was calculated as a non-linear combination of the latter two indicators, thus resulted in a close to sustainable value of 0.45. It was clearly demonstrated that these metrics are suitable for environmental assessment of chemical synthesis, and the results pointed out the importance of high conversion and selectivity of reaction steps, and the weakness of waste handling.

INTRODUCTION

The uncertain date of depletion of fossil resources shifted the focus of interest of energy generation and fuel production towards renewables. Renewable resources are quite diverse, but biomass is the only resource from which biomass-based liquids can be produced. Several chemicals called Intermediate Platform Chemicals (IPCs) could be produced from biomass via its biochemical or physicochemical conversion (Mika, L.T., Cséfalvay, E., & Németh, Á. (2018)). However, the only long-term existing and huge-quantity-produced candidate is bioethanol. Recent commercial interests have focused on bioethanol and biodiesel, as illustrated by the continuing growth in their production (EIA (2012); IEA (2019). World's 2001 year bioethanol production of 31 billion litres increased to 110 billion liter in 2018 and further growth is estimated up to 130 billion in year 2024

(IEA (2019)). Brazil and the US are the world-leading producers; their ethanol output represents two thirds of the world's total bioethanol production (Kulman, K. (2017)). In spite of being a small country, Hungary produces significant amount first-generation bioethanol (approx. 500 million litres) (Balla, Z. (2013)). Lignocellulosic residues such as wheat straw or corn stover represent the feedstock of second-generation bioethanol production. By the addition of second-generation bioethanol (or cellulosic ethanol) production, the overall ethanol yield can be increased by about 20% (Balla, Z. (2013); Groode, T.A. (2008)). Another potential resource of bioethanol production could the lignocellulosic waste of agriculture or forestry, shifting the balance positively, since the utilisation of waste does not influence the field usage and compete with food production (Bjerre, A.B. et al. (1996)). Estimations predicted another annual production of 442 billion litres of ethanol from the lignocellulosic residues of the food industry, and further 491 billion litres from other plant wastes (Kim, S. & Dale, B.E. (2004)).

The first application of bioethanol as fuel-additive is dated back to 1926 in Hungary, due to fuel shortages. Fermented alcohol was blended at 20% with gasoline and the mixture was marketed under the name 'Motalko' (Bai, A. (2013)). A similar situation was occurred in the 1930s in Germany. Due to the oil-deficient at that time a mixture called 'Kraftspirit' was used as fuel, which contained 10% alcohol (Kovarik, W. (2021)). Then in 2005, an EU-wide directive was introduced on the widespread use of bioethanol as a fuel component (European Parliament & Council of the European Union (2003)). The utilisation of bioethanol as the starting material in the production of basic chemicals was proposed only in 2017 (Horváth, I.T. et al. (2017)). The study revealed that in spite of the theoretical feasibility, it is not economically viable due to the vast quantity of basic chemicals and the limited amount of ethanol as a resource. As the feedstock volume seems to be the limiting factor, our suggestion is to use bioethanol for the production of chemicals produced in small quantities, such as lighter fluids or fuel-additives. Comparing the consumptions of lighter fluids (LFs) with commodity chemicals, they are produced in limited volumes (only kilotonnes), while basic chemicals such as ethylene are sold in high volumes (million tonnes). According to an assessment including grill lighter fluids published the European Chemicals Agency (ECHA) grill lighter fluid 2013 year consumption in Norway and Finland were reported as follows: 1 230 and 470 metric tonnes for Norway and Finland, respectively (ECHA (2015), Table 3). These data clearly indicates that charcoal lighter fluids represent a small volume against commodity chemicals. Consequently, the production of lighter fluids on biomass basis can be proposed as a viable and even environmentally friendly alternative. A recent paper summed up the typically fossil-based lighter fluids and their possible biomass-based alternatives and pointed out that the latter have attractive properties: higher flash point, lower vapour pressure and lower toxicity than those of fossil-based lighter fluids (Cséfalvay, E. (2018)). A possible bio-based lighter fluid could be the mix of 30 wt% biodiesel and 70 wt% *n*-butanol having flash point reduced volatile organic compound (VOC) emissions (U.S. 9084507 patent, (2015)). Beside its prosperous use as a bio-based LF component, *n*-butanol was also proposed and tested as a possible diesel additive and

used as a blending compound to reduce particulate matter (PM) emission in the exhaust gases of diesel combustion engines. It was revealed that blending 5–10 v% of *n*-butanol to diesel reduces both the PM and CO_2 emissions of the mix, while keeping the engine performance at the same level (Lujaji, F. et al. (2011)). As long as vehicles with internal combustion engines are in the transport, research on blending components is required. Thus, *n*-butanol seems to be a prosperous compound of biomass-based lighter fluids as well as an attractive blending component of diesel.

The classical route to produce bio-butanol from sugar (Chen, C. et al. (2014)), glycerol (Yadav, S. et al. (2014)) or lignocellulose (Yang, M. et al. (2014)) is the acetone-butanol-ethanol fermentation (ABE fermentation) by using Clostridium strains (Ezeji, T. et al. (2010)). Enzymes ferment the biomass-origin sugar as feed to acetone, butanol and ethanol, under mild conditions. However, the yield is moderate compared to other synthetic methods. Bio-butanol production via fermentation from glycerol is also considered as an alternative route, because huge amount of glycerol is formed as a by-product of biodiesel production. In the glycerol fermentation process butanol is the main product, however, the side-products' (acetone and ethanol) removal from the mixture makes the process less efficient (Ndaba, B., Chyjanzu, I. & Marx, S. (2015)). Another, synthetic route for butanol production is based on the fermentation of synthesis gas (Worden, R.M. et al. (1991)) that originates from fossil resources. Noteworthy, synthesis gas can also be produced from biomass (Rauch, R.H. (2014)) but as we are dedicated to use bioethanol, we focus on *n*-butanol production from bioethanol as a feedstock.

We propose here a novel synthesis method of *n*-butanol from bioethanol as a starting material. Taking into consideration conversion, selectivity and overall yield, chemical conversion would be more efficient than enzymatic fermentation. Bioethanol is produced from biomass at industrial scale for long and it is readily available, it could be used as a feedstock of *n*-butanol production.

THE PROPOSED MECHANISM TO PRODUCE *N*-BUTANOL FROM BIOETHANOL

The five-step chemical synthesis of *n*-butanol from ethanol is illustrated in Figure 1.

Step 1: Dehydration of ethanol to ethene

The chemical dehydration is carried out with a homogeneous catalyst of sulfuric acid or phosphoric acid at a temperature of about 300°C. Depending on the temperature and the catalyst chosen, selectivity of the synthesis can reach up to 99% at 100% conversion. Modern systems already use solid catalysts such as aluminium, silicon, manganese and iron oxides, special zeolites and several solid acid catalysts have also been found in the literature (Ulmann (2011)). The reaction is an elimination reaction in which water and ethene are obtained. The latter is further converted.

Step 2: Wacker synthesis (oxidation) to acetaldehyde

Acetaldehyde production is already well known in the industry. Ethene is oxidised in the liquid phase using a homogeneous Pd-Cu catalyst system. The reaction is cocatalysis and typically performed in an

aqueous solution by using $PdCl_2$ and $CuCl_2$ as catalysts. The conversion of this step is typically 80–82% with a selectivity of 98% (Okamoto, M. & Taniguchi, Y. (2009)); (Carey & Sundberg, (2007)).

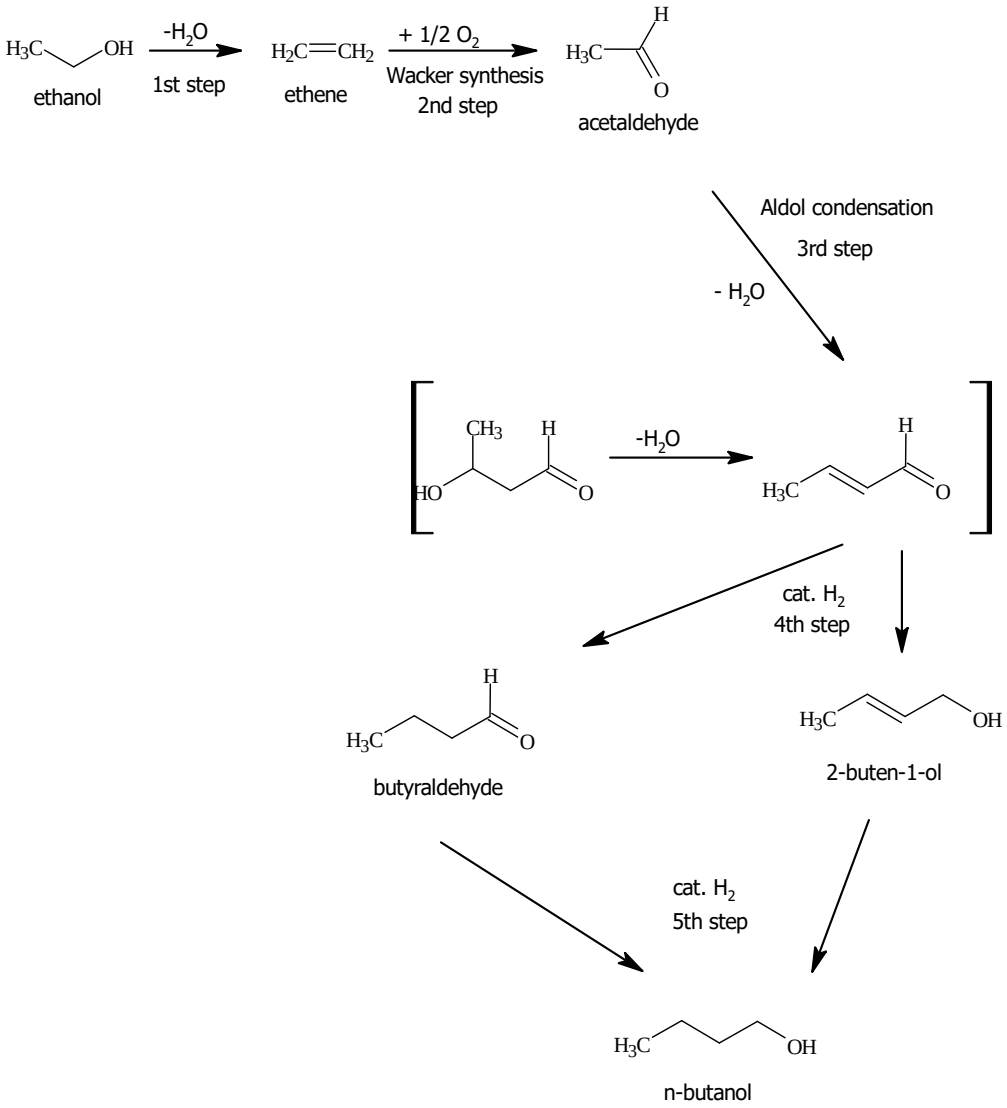

Fig. 1. Synthesis of *n*-butanol from ethanol

Step 3: Aldol condensation for α-hydroxyaldehyde and α-hydroxyketone

Aldol condensation is generally described as the method used to produce α-hydroxyaldehyde or α-hydroxyketone. In addition, aldol condensation is an important organic chemical synthesis method that has the advantage of forming carbon-carbon bonds (Carey, F.A. & Sundberg, R.J. (2007)).

Steps 4-5: Catalytic hydrogenation to n-butanol

The next step after aldol condensation is the hydrogenation of aldol adducts to increase their solubility in water. Thermodynamic conditions allow hydrogenation of the C = C bond in hydrogenation reactions containing unsaturated aldehydes instead of

the C = O bond. Reaction kinetic conditions also allow hydrogenation of the C = C bond over the C = O bond for small molecules. While steric hindrances for larger molecules reduce the degree of hydrogenation of C = C bonds, *n*-butanol is synthesised via the hydrogenation butyraldehyde and 2-buten-1-ol. The conversion of the aldol condensation and hydrogenation steps is 80% and the selectivity is 99% (Carey, F.A. & Sundberg, R.J. (2007)).

Yield of each reaction step is calculated by multiplying the related conversion and selectivity values; the yield of the gross reaction is obtained by multiplying the yields of every individual step, and equals 63% (see Table 1).

Step	Reaction steps to convert ethanol to *n*-butanol	Reaction	Ref.
1	$\mathbf{2\ CH_3-CH_2-OH \rightarrow\ 2\ CH_2=CH_2+2\ H_2O}$	*Dehydration* Conversion: 100% Selectivity: 99% Yield: 99.0%	Ulmann (2012)
2	$\mathbf{2\ CH_2=CH_2\ +\ O_2 \rightarrow\ 2\ CH_3-CHO}$	*Oxidation* Conversion: 82% Selectivity: 98% Yield: 80.36%	Sano, K., Uchida, H. & Wakaba-yashi, S. (1999)
3	$\mathbf{2\ CH_3-CHO \rightarrow\ x\ CH_3-CH=CH-CH_2+}$ $+\ \mathrm{y\ CH_3\text{-}CH_2\text{-}CH_2\text{-}CHO\ +\ H_2O}$ *,where x+y=1*	*Aldol-condensation & hydrogenation* Conversion: 80% Selectivity: 99% Yield: 79.2%	(Carey & Sundberg (2007))
4	$\mathbf{x\ CH_3-CH=CH-CH_2+\ y\ CH_3-CH_2-CH_2-CHO+H_2 \rightarrow}$ $\mathrm{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH}$ *,where x+y=1*		
Gross reac-tion	$\mathbf{2\ CH_3-CH_2-OH+\ O_2+H_2 \rightarrow\ CH_3-CH_2-CH_2-CH_2-OH+\ 3\ H_2O}$ $\mathbf{2\ CH_3-CH_2-OH+\ O_2+H_2 \rightarrow\ CH_3-CH_2-CH_2-CH_2-OH+\ 3\ H_2O}$	Total yield: 63.0%	

Table 1. Bioethanol-based production of *n*-butanol

An earlier review (Ndaba, B., Chyjanzu, I. & Marx, S. (2015)) discussed the bio-chemical and chemical routes of the synthesis of *n*-butanol from ethanol. Considering the chemical routes, dehydrogenation of ethanol to form acetaldehydes, followed by aldol condensation of acetaldehyde and then hydrogenation to *n*-butanol was proposed as an efficient synthesis method to produce *n*-butanol. For the improvement of the reaction yield, research is focused to develop appropriate catalysts; their selectivity to *n*-butanol varies between 10–80%. According to our knowledge yield calculated as the product of conversion and selectivity better describes the efficiency of a reaction (and the catalyst used). Selectivity of our proposed reactions reach 99% in step 1 (dehydration of ethanol), 98% in step 2 (oxidation), and 99% in steps 3 and 4 (aldol condensation and hydrogenation). In spite of the high selectivity of each step, the gross reaction's yield is 63% for *n*-butanol, due to the imperfect conversion values. Although the overall yield seems to be a moderate value, recycling of the initial compounds in each reaction step can help improving the conversion thus the yield. Compared to the results summarised in a 2015 review (Ndaba, B., Chyjanzu, I. & Marx, S. (2015)), our proposed synthesis

route shows excellent selectivity but a moderate yield of 63% for the gross reaction.

EVALUATION OF THE *N*-BUTANOL PRODUCTION ROUTE USING ETHANOL EQUIVALENT AND SUSTAINABILITY METRICS

Our suggested route incorporates two processes: ethanol production from biomass, and *n*-butanol production from ethanol. In order to assess sustainability of the multistage reaction fate of wastes should also be taken into account.

Ethanol equivalent (EE) is proposed for the comparison of fossil and biomass-based materials or products, giving the mass of ethanol required to cover the equivalent amount of energy that can be extracted from a given raw material source and the mass of ethanol that can produce the equivalent amount of mass of a given carbon-based chemical using molar equivalency (Csefalvay, E. et al. (2015)).

We need a significant amount of energy to produce ethanol from biomass, which – in a sustainable world – would be also covered from bioethanol. Based on these, an *actual ethanol equivalent (EE_x)* can be defined, which also includes the bioethanol production efficiency, in other words *ethanol return on ethanol (ERoE)*, i.e. the number of bioethanol units (x) produced per 1 unit of bioethanol consumption. Using the actual ethanol equivalent, the amount of biomass (e.g. corn) and the size of the land required for cultivation can be calculated. For example, if 1 unit of energy is used to fertilise, spray, use agricultural machinery, ferment, distillate, etc., it is calculated that four times as much energy is obtained with it in the form of ethanol. Thus, the abbreviation EE_4 refers to a 4-fold ratio i.e. by using 1 unit of energy input the extracted energy equals 4. The ERoE measure plays a major role in the reproduction of resources, with a numerical value of 2.3 before 2016 for the first generation bioethanol; as of 2016, it is 4.0. As the technology advances, this number can be further increased (Shapouri, H. et al. (2010)).

Focusing on another important factor of sustainability, the *fate of waste* must also be taken into account. Materials used from the ecosphere can be transformed into useful products and waste can be recycled back into the ecosphere. As Mark de Swaan Arons emphasized a sustainable technology should not emit any harmful products at all. As the generation of waste cannot be completely avoided, the assessment of the technology's sustainability must also take into account the waste treatment, either by natural decomposition or by the use of artificial technologies. Several green chemical indicators are known to describe chemical reactions and technologies. The two simplest indicators are the Trost's *atomic efficiency index* (see equation (**1a**)) (Trost, B.M. (1991)) and the Sheldon *e-factor* (environmental factor (see **1b**)) (Sheldon, R.A. (1994)) described by the formulas (1a) and (1b).

Several metrics can be used to assess the sustainability of carbon-based chemicals through resource and waste issues. We determine the *sustainability value* of resource reproduction metric (SV_{rep}) and sustainability value of the fate of the waste metric (SV_{waste}) to establish a *sustainability index* (SUS_{ind}) to assess the sustainability of biomass-based chemicals. It is important to emphasise that the indicators are based on the ethanol equivalent to bring all types of carbon-based compounds into a comparable range using the carbon atom equivalent (Csefalvay, E. et al. (2015)). In the synthesis of a product, it must be

considered whether another process does not produce the actual product as a by-product, which could be used as a secondary source ($EE_{secondary\ sources}$).

$$Atom\ Efficiency = \frac{M_{product}}{\sum M_{starting\ material}} \times 100\% \quad \textbf{(1a)}$$

$$E - factor = \frac{mass\ of\ total\ waste}{mass\ of\ product} \quad \textbf{(1b)}$$

The *lifetime of a given substance* ($t_{lifetime}$) contributes to the sustainability of resource reproduction, which tells us how long it takes to consume the necessary resources, which is usually 1 year due to the annual cycle of the economy. The *reproduction time* ($t_{reproduction}$) shows how long it takes to produce the available resources, which is 1 year, taking into account the environmental conditions of corn crop production in the continental climate. After that $\mathbf{SV_{rep}}$ can be calculated according to equation **(2)** (Horváth I.T. et al. (2017)):

$$SV_{rep} = \frac{\frac{ERoE}{ERoE+1} \times \frac{ERoE}{4} \times EE_{avaible\ resource} + EE_{secondary\ resource}}{\frac{t_{replacement}}{\frac{EE_{necessary\ resource}}{t_{consumption}}}} \quad (\mathbf{2})$$

If $\mathbf{SV_{rep}}$ equal to or greater than 1, the rate of reproduction of the sources is greater than the rate of their use, so it is sustainable in terms of reproduction.

In addition to reproduction, products must be examined for their interaction with the environment. The amount of waste generated is also calculated in ethanol equivalent (EE_{waste}). *Considering the treated and untreated status of the waste, their equivalent weight of ethanol (*$EE_{treated\ waste}$ and $EE_{untreated\ waste}$) can be calculated. The sustainability metric introduced for waste must include the *time of waste generation* ($t_{waste\ generation}$), which is 1 year due to its cyclicality. After the waste has been released into the nature, their compounds start to degrade naturally. Assuming the worst outcome, the longest half-life of the given waste chemical was used in our assessment (half-time is the time required for a quantity to reduce to half of its initial value). A compound is considered to be degraded if its concentration drops to or under 0.1% of the released concentration, therefore, the decomposition time of the waste ($t_{waste\ decomposition}$) is determined by taking into account the time during which the waste generated during the synthesis of the product falls below the concentration limit in addition to the 1 year of release (Cséfalvay, E., Hajas, T. & Mika, T.L. (2020)).

By knowing the quantities defined above, $\mathbf{SV_{waste}}$ can be calculated in physical meaning and is a condition for sustainability on the waste side, that no waste accumulates, i.e. the rate of waste loss is greater than or equal to the rate of waste generation. This is expressed by the

following equation **(3)** (Horváth, I.T. et al. (2017)):

$$SV_{waste} = \frac{\frac{EE_{treated\ waste} + EE_{untreated\ waste}}{t_{waste\ treatment} + t_{waste\ natural\ decomposition}}}{\frac{EE_{generated\ waste}}{t_{waste\ generation}}} \textbf{(3).}$$

From the equations **(2)** and **(3)** it is already possible to calculate **the sustainability index (SUS_{ind})**, which takes into account the individual indicators with a non-linear weighting for the pattern of coupling of the parallel resistors, therefore equation **(4)** is as follows (Horváth, I.T. et al. (2017)):

$$\mathrm{SUS_{ind}} = \frac{\mathrm{SV_{rep}} \cdot \mathrm{SV_{waste}}}{\mathrm{SV_{rep}} + \mathrm{SV_{waste}}} \textbf{(4).}$$

RESULTS AND DISCUSSION

Environmental sustainability assessment was started with the calculation of the atom efficiency according to eq. (**1a**). *E-factor* was calculated according to eq. (**1b**): waste was determined for each reaction steps by using the 'conversion × (1–selectivity)' equation as for waste ratio calculation, then they were summarised to have the total waste generated. Finally the mass of the total waste was compared to the mass of the product:

$$Atom\ Efficiency = \frac{M_{n-butanol}}{2 \times M_{ethanol} + M_{oxygen} + M_{hydrogen}} \times 100\% = 58.8\%$$

The results are summarised in *Table 2*.

Indicators	**Results in the production of *n*-butanol from ethanol through the proposed method (see Fig. 1.)**
E-factor	0.8914
Atom efficiency	58.8 %

Table 2. Green chemical indicators of the production of *n*-butanol from ethanol

For comparison the E-factor related to the pharmaceutical industry is high, even higher than 100 kg waste/kg product. The typical ranges for fine chemicals' production, bulk chemicals' production and oil refinery are 5–50, 1–5 and <0.1 kg waste/kg product, respectively (Sheldon, R.A. (1994)). Higher E-factor means more

waste is generated and greater the negative environmental impact. The ideal E-factor is zero, when no waste is generated. Our analysis shows that the E-factor of 0.8914 (see Table 2) for our proposed method is attractive from environmental point of view. The results clearly indicate that the material balance is shifted towards the product.

Taking into account the gross reaction, 2 moles ethanol are required as carbon-source for the production of 1 mol *n*-butanol, and additionally 1 mol oxygen and 1 mol hydrogen are also essential reagents. The gross reaction seems to be moderately *atom efficient* with its 58.8%. Noteworthy 2 moles of water are formed as by-products of the reaction and this valuable amount of water is not included in the approach of atom efficiency. Further calculations are derived according to the guide of Horváth et. al. and available in detail in the electronic supplementary information of the named reference (Horváth I.T. et al. (2017)).

For the environmental sustainability evaluations, we selected EU consumption statistics: 0.67 mt butanol was consumed in the EU-28 in 2015 (Eurostat (2021)). Considering a possible production of this amount of *n*-butanol from ethanol via our proposed mechanism 2.97 mt ethanol would be required to account for all the carbon atoms including 63% yield (see *Table 3*). Regarding an exotherm gross reaction, the reaction enthalpy itself appears to be negative, and taking into account the ethanol's energy content, the reaction enthalpy can be turned to ethanol equivalent and results in -0.314 mt EE. As a sum of EE of carbon-atom equivalency and reaction enthalpy an overall 2.66 mt EE is required to produce 0.67 mt *n*-butanol. In comparison with EU-28's ethanol production 5 399 million liters i.e. 4.26 mt ethanol was produced in 2015, which is almost double than the necessary amount. Thus, SV_{rep} appears to be 5.15 and much over 1, which is the limit of

Sustainability metrics	**Results**
Ethanol equivalent (EE) of *n*-butanol based on carbon-atom equivalency	**2.97 mt EE**
Ethanol equivalent (EE) of the standard enthalpy of reaction	**- 0.314 mt EE**
$EE_{necessary\ resource}$	**2.66 mt EE**
SV_{rep}	**5.15**
SV_{waste}	**0.49**
SUS_{ind}	**0.45**

Table 3. Results of sustainability metrics for *n*-butanol production based on bioethanol

sustainability of resource replacement. We can state *that we do have enough ethanol to use as a biomass-based starting material to produce chemicals, such as n-butanol.*Considering the waste issue, we identified each compound formed as waste in each reaction steps and collected their half-lives in the environment (see Table 4). We assumed that only the waste produced in step 1 is released into the environment. Our approach was to use the longest half-life, i.e. 39 h in lake in case of reaction step 1, and waste decomposition time was set to the 0.1% of the initial concentration over 1 year of production. In case of steps 2, 3 and 4 crotonaldehyde, methyl-acetate, butyraldehyde, crotyl-alcohol are received as waste. Although they seem to be valuable compounds, their recovery would make the process more complicated, and because of their low yields it would be a useless exercise. Thus, we assumed that these compounds are purged and burnt immediately, consequently the treatment time equals one year. As using 30% of the waste is released without treatment and 70% is incinerated, 0.49 is calculated for SV_{waste}, which is below the sustainable value (i.e. $SV_{waste} = 1$).

Because SUS_{ind} is calculated as non-linear weighting, the lower indicator governs its value resulting in 0.45. To be sustainable we should have reach or overcome 0.5, so it can be concluded that *the production of n-butanol from bioethanol is currently not sustainable from environmental point of view*. As the conversion values of each reaction steps are improved, SV_{waste} could also be increased but never reaches the limit of sustainability (i.e. $SV_{waste} = 1$) unless all reaction steps work with 100% conversion and 100% selectivity. A possible way to reach the desired limit would be separation and utilisation of the received wastes as valuable compounds elsewhere.

Steps		**Wastes**	**Photocatalytic decomposition in air**	**Half-life of volatilisation from water**		**Half-life of biodegradation**	
				river	**lake**	**water**	**soil**
Step 1	Ethanol dehydration	Oxygenates[1]	36 h	5 h	**39 h**	n/a	few days
Step 2	Ethylene dimerisation	crotonaldehyde[2], methyl-acetate[3]	11 h	40 h	15 days	n/a	n/a
Step 3-4	Aldol condensation and catalytic hydrogenation	butyraldehyde, crotyl-alcohol[4]	16 h	9 h	5 days	n/a	n/a

Table 4. By-products formation during the synthesis of *n*-butanol, and their half-lives in different environment from Pubchem database (see footnotes)

[1] http://pubchem.ncbi.nlm.nih.gov/compound/702#section=Ecological-Information. [accessed on 20 October 2020]
[2] https://pubchem.ncbi.nlm.nih.gov/compound/6584#section=Ecological-Information. [accessed on 20. October 2020]
[3] https://pubchem.ncbi.nlm.nih.gov/compound/447466#section=Ecological-Information. [accessed on 20 October 2020]
[4] https://pubchem.ncbi.nlm.nih.gov/compound/261#section=Ecological-Information. [accessed on 20 October 2020].

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CONCLUSIONS

All in all, we propose a novel route to produce *n*-butanol from bioethanol via four steps: step 1: dehydration of ethanol; step 2: Wacker synthesis (oxidation); step 3: aldol condensation; and step 4: hydrogenation. The novelty of the work is to lead the reaction via the dehydration of ethanol to ethene, which step has attractive high conversion (100%) and selectivity (99%) values, moreover water forms as a by-product, which makes the whole process environmentally friendly. Based on the environmental sustainability assessment we concluded that the resource is not a limiting factor, we do have enough ethanol as a raw material for the production of *n*-butanol. Considering the atom efficiency, 58.8% was revealed for the gross reaction. It should be noted that 2 moles water form as by-product of the reaction and this valuable amount of water is not included in the approach of atom efficiency. Regarding the waste issue our proposed method is very close to those of oil refinery processes representing a very low E-factor. In spite small amount of waste generation, their treatment is not solved completely, thus worsening the SV_{waste} value. It can be concluded that *the weakness of the process is the waste treatment issue*, thus making the whole process unsustainable ($SUS_{ind} = 0.45 < 0.5$).

ACKNOWLEDGEMENT

Edit Cséfalvay is grateful for the financial support to Budapest University of Technology and Economics (BME) providing ÚNKP-20-5-BME-162 scholarship, and János Bolyai Research Scholarship (BO/00706/17/6) of the Hungarian Academy of Sciences. The research reported in this paper and carried out at BME has been supported by the NRDI Fund (TKP2020 NC, Grant No. BME-NC) based on the charter of bolster issued by the NRDI Office under the auspices of the Ministry for Innovation and Technology.

Keywords: bioethanol, *n*-butanol, environmental sustainability assessment, E-factor, Ethanol Equivalent, sustainability metrics

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